ON THE VIBRATIONAL SPECTRA OF SOME MONO-SUBSTITUTED BENZENE COMPOUNDS

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(Plate 16)

ABSTRACT. The Raman spectra and the state of polarization of the Raman lines of benzyl formate have been reported, apparently for the first time. The infrared spectrum of benzyl formate and the Raman and infrared spectra of benzaldehyde and benzoyl chloride have also been investigated. Assignment of the vibrational frequencies of benzaldehyde and benzoyl chloride reported by previous authors has been critically examined and alternative assignment for some of the frequencies has been suggested. Complete assignment of the observed vibrational frequencies of benzyl formate to different modes of vibration has also been proposed.

INTRODUCTION

The Raman spectra of benzaldehyde and benzoyl chloride were earlier studied by a number of workers (Pertrikaln *et al*, 1929; Dadieu *et al*, 1929; Pal *et al*, 1930; Lu, 1931; Matsuno *et al*, 1933; Herz *et al*, 1943; Sirkar *et al*, 1946; Herz *et al*, 1947; Chiorbori *et al*, 1951; Biswas, 1956; Gilbert, 1959). Apparently the Raman spectrum of benzyl formate was not reported earlier and is being reported for the first time along with the polarisation data.

Garrigou-Lagrange *et al* (1961) investigated the infrared spectra of benzaldehyde and benzoyl chloride and assigned the fundamental vibrational frequencies to different modes. No assignment for benzyl formate is, however, available in the literature. In the present work it was therefore proposed to undertake reasonably complete assignment of fundamental frequencies of benzyl formate and also to examine the assignments proposed by Garrigou-Lagrange *et al.* for benzaldehyde and benzoyl chloride molecules. With this end in view, the Raman spectra of benzaldehyde and benzoyl chloride were reinvestigated and the infrared spectra of all the three compounds were also recorded. The Raman shifts of benzaldehyde and benzoyl chloride and their polarisation data are given in the tables of Landolt-Börnstein (1961) and Magat (1936) but there are some discrepancies in the values of depolarisation factors of some of the Raman lines published in these tables. So, the polarisation characters of the lines were qualitatively reinvestigated. The proposed assignments of the observed frequencies have been discussed in the present paper.

EXPERIMENTAL

The samples of benzyl formate, benzaldehyde and benzoyl chloride were of chemically pure quality, supplied by B.D.H. They were fractionally distilled and the proper fractions after being collected were repeatedly distilled under reduced pressure before use.

The Raman spectra and the states of polarisation of the Raman lines were studied in a manner described in a previous paper (Chattopadhyay *et al*, 1966). The infrared spectra of the compounds in the liquid state and in dilute solutions were recorded in the usual way with a Perkin-Elmer Model 21 spectrophotometer fitted with rock salt optics.

RESULTS AND DISCUSSIONS

Raman and infrared data are given in tables 1, 2, and 3 and the proposed assignments of the frequencies due to the phenyl ring and those due to the substituent groups have been summarised in tables 4 and 5 respectively. As mentioned above, the polarisation data of benzaldehyde and benzoyl chloride were reinvestigated. The observed polarisation characters of some of the Raman lines were found to be in better agreement with the factors of depolarisation of these lines given in Magat's tables and the latter have been included in the tables 2 and 3 along with the data taken from Landolt-Börnstein tables. The Raman spectrum and the infrared absorption curve due to benzyl formate are reproduced in figures 1 (Plate 16) and 2.

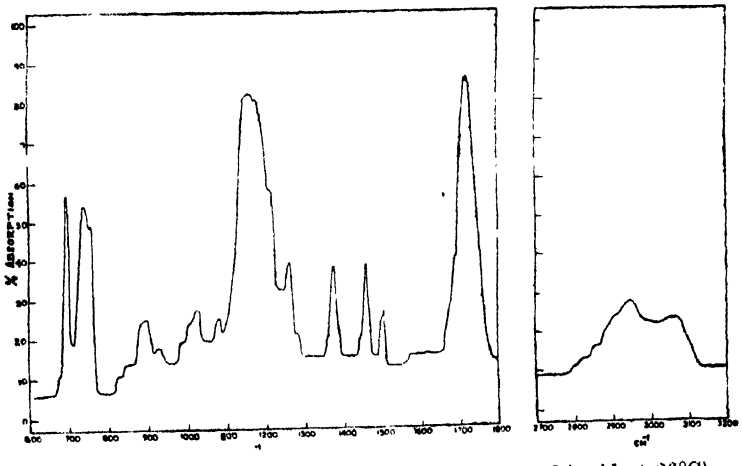

Figure 2. Infrared spectra of Benzyl Formate (Liquid at 26°C)

The molecules of benzaldehyde and benzoyl chloride, which may be reasonably assumed to be planar, belong to C_s point group. Similarly, the molecule of benzyl formate may belong to the point group C_s if in addition to the element of identity which it possesses, the plane of the phenyl ring is assumed to be a plane of symmetry. Then treating the substituent group as a single unit X, in each mole-

cule there will be thirty vibrational modes characteristic of the phenyl ring which will be distributed among two different symmetry species as $21a'+9a''$. In addition, there will be extra modes, 18 in the case of benzyl formate and 6 in the case of each of the other two molecules, arising from vibrations and the rotational motions of the substituent group. However, it may be remembered that the Raman and infrared activity and polarisation character of some of the phenyl ring vibrations would depend on the symmetry of the ring only (Horak *et al*, 1967; Chattopadhyay, 1968). The vibrations of the phenyl ring and the substituent groups are discussed separately in the following paragraphs.

A. *Vibrational modes of the phenyl ring.*

1. *Benzyl formate* : It can be seen from Table 4 that most of the fundamental modes of the ring could be identified with the observed Raman and infrared bands. Some of the assignments have been discussed below.

In the Raman spectrum there is a strong broad polarised line at 3060 cm^{-1} while in the infrared spectrum a medium broad band at 3060 cm^{-1} is observed. Because of inadequate dispersions of the instruments, probably freauencies due to the different C—H stretching modes of benzene which have close values have not been resolved from each other and the assignments of these frequencies are tentative. The Raman spectrum of benzyl formate exhibits a strong polarised line at 1216 cm^{-1}. The corresponding infrared band is also of large intensity. Bands of similar characteristics at 1202 and 1203 cm^{-1} are also observed in the Raman and infrared spectra of benzaldehyde and benzoyl chloride respectively. As discussed by Sirkar and Bishui (1968a) a suitable localised oscillation may be responsible for the origin of the observed frequency in this region. The ring breathing mode is readily recognised in the strong and polarised Raman line at 1000 cm^{-1} which appears as a weak band in the infrared spectrum. As discussed by Whiffen, in the case of monosubstituted benzene C_6H_5X belonging to the point group c_{2v}, the mode is a trigonal a_1 mode (p). There is another trigonal breathing mode r which involves in-phase motion of the substituent group. Therefore, the polarised Raman line at 823 cm^{-1} may reasonably be assigned to this mode. One component (6B) of the e_g^+ mode 6 of benzene which hardly changes on substitution has been assigned at the frequency 620 cm^{-1} which appears strongly in the Raman effect. The other component, 6A which is sensitive to substitution has been identified with the Raman shift 481 cm^{-1}. Frequencies corresponding to modes 4, 16A and 16B could not be observed in the Raman spectrum.

The remaining frequencies may be assigned to different modes as shown in Table 4.

2. *Benzaldehyde and benzoyl chloride*:

As indicated in table 4, most of the observed frequencies may be assigned to different vibrational modes of the benzene ring in a straightforward way.

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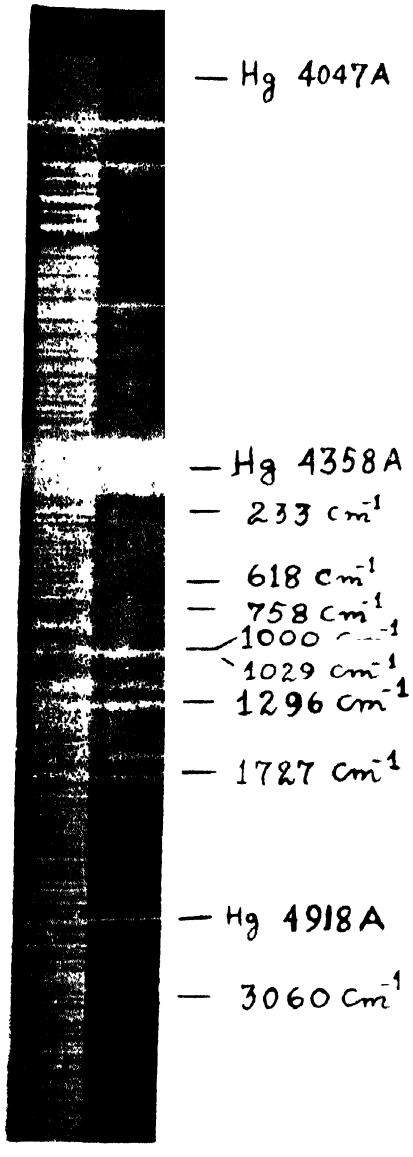

Figure 1. Raman spectra of Benzylformate (liquid at 28 C)

Garrigou-Langrange *et al* (1961) had previously assigned the vibrational frequencies of these molecules to different modes. But on careful examination it was found necessary to revise some of the assignments proposed by them in order to explain the observed intensities of the corresponding bands in infrared and Raman spectra and the polarisation character of the Raman lines. Some of the features of the assignment have been discussed below.

The Raman spectrum of benzaldehyde clearly exhibits frequency shifts of 1003 cm^{-1} and 830 cm^{-1} arising from the trigonal modes *p* and *r* (Whiffen, 1966) respectively. Garrigou-Lagrange *et al* (1961) assigned the 826 cm^{-1} band to an out-of-plane C—H bending mode. But the high degree of polarisation of this band in the Raman spectrum clearly supports the present assignment. In the case of benzoyl chloride there is no Raman line in the 820-830 cm^{-1} region. Instead, there is a strong polarised line at 673 cm^{-1}. Since in mode *r*, the substituent moves with appreciable amplitude, the corresponding frequency would be lowered considerably if the $C\begin{matrix}O\\ \diagup\\ \diagdown\\ Cl\end{matrix}$ group moves as a whole during the execution of this mode. In fact, in monohalobenzenes this frequency falls off considerably in going from fluorine to iodine (Whiffen, 1956). Thus the frequency 673 cm^{-1} may be reasonably assumed to arise from this mode and has been assigned as such. In benzoyl chloride, there is another polarised Raman line of frequency shift 507 cm^{-1}, but this frequency appears to be too low to be assigned to this mode. Similarly, the X-sensitive mode 6A (corresponding to Whiffen's mode *t*) which also involves considerable motion of C—X group has been assigned to the polarised Raman line of frequency shift 312 cm^{-1} observed in benzoyl chloride and the line at 442 cm^{-1} observed in benzaldehyde. The Raman spectra of both the compounds exhibit frequency shifts of about 650 cm^{-1} which probably arise from mode 4. In the case of benzaldehyde, and also of benzoyl chloride, there is a strong infrared band at 685 cm^{-1} the corresponding Raman line being absent and this frequency has been assigned to mode 11. Garrigou-Lagrange *et al* (1961), however, attributed to this mode the infrared band due to benzaldehyde at 741 cm^{-1} which appears with moderate intensity in the Raman spectrum and is depolarised. But this mode would be expected to be strongly active only in the infrared and the present assignment of the 685 cm^{-1} band to this mode appears to be more reasonable. The 741 cm^{-1} band (779 cm^{-1} in the case of benzoyl chloride) has, on the other hand, been assigned to the mode 17B which would belong to b_2-species for C_{2v} symmetry. This mode would give rise to depolarised Raman line and would also be active in the infrared. The Raman and infrared activity and the polarisation character thus favour the assignment of the 741 cm^{-1} band to mode 17B mode in the present paper.

The frequency observed in the case of monosubstituted benzenes in the 1020-1030 cm^{-1} region is usually associated with the mode *b* corresponding to the mode

18A of benzene (Whiffen, 1956). But Sirkar and Bishui (1968a) recently pointed out that the value is rather too high for this mode and also the large intensity of the corresponding Raman line and its low depolarisation factor are inconsistent with the symmetry of this mode. These authors described an alternative mode in which there is breathing motion of the six carbon atoms of the ring and a simultaneous stretching of the C—X bond. They suggested that this mode may be responsible for the Raman shift observed in this region in the case of mono-substituted benzenes. In addition, benzoyl chloride yields a depolarised Raman line of frequency shift 415 cm^{-1} which has been attributed to mode 16A. Further, in the Raman and infrared spectra of benzoyl chloride some of the bands due to C—H stretching vibrations have been resolved from each other.

VIBRATIONS IN THE SUBSTITUENT GROUPS

(i) *Carbonyl frequency* : In the Raman and infrared spectra of both benzyl formate and benzaldehyde only one band arising from carbonyl bond stretching vibration is observed in the usual position. In the case of benzoyl chloride, however, two frequencies at 1730 and 1771 cm^{-1} have been observed. According to the generally prevailing idea this splitting of the crabonyl bond stretching frequency is due to 'Fermi Resonance' between the carbonyl vibration and a close lying overtone of a suitable vibrational frequency (Rao *et al*, 1962; Yoshida, 1962). But according to Forbes and Myron (1961) the doublet may occur because of an intermolecular vibration, the exact mechanism of which, according to them, requires furter study. Recently, Sirkar and Bishui (1968b) discussed the possibility of an alternative explanation of the splitting on the basis of two possible configurations of benzoyl chloride molecule. In the present investigation no attempt has been made to offer any explanation.

(ii) *C—H vibrations* : In making assignments of vibrations in the CH_2 group in benzyl formate, guidance has been taken from results discussed by previous authors (Brown and Sheppard, 1950; Brown *et al* 1950; Sheppard *et al*, 1953). The frequencies due to stretching in the CH_2 group generally occur in the region 2800-3000 cm^{-1} and two infrared bands of moderate intensity at 2905 and 2950 cm^{-1}, both of which appear also in the Raman spectrum, are assigned to symmetric and asymmetric modes respectively. Of the two frequencies 1260 and 1155 cm^{-1}, the higher one is attributed to the wagging mode and the lower one to the twisting mode. The CH_2 rocking mode is identified with the strong infrared band at 738 cm^{-1}. The CH_2 scissoring mode, expected in the 1450 cm^{-1} region, is identified with 1448 cm^{-1} band.

The C—H stretching mode due to the formyl group in benzyl formate is assigned at 2950 cm^{-1} following Wilmshurst (1957). The in-plane and out-of-plane CH ceformation vibrations were observed by Wilmshust (1957) in methyl formate at 1371 and 1032 cm^{-1} respectively. Accordingly, the bands observed

in similar positions in the present investigation have been assigned to in-plane and out-of-plane C—H bending vibrations.

Colthup (1950) quotes the range 2700-2900 cm^{-1} for the C—H valence vibration when the hydrogen atom is attached to a crabonyl group. But Pozefsky *et al* (1951) found two bands near 2720 and 2820 cm^{-1} for a number of aldehydes. In the present investigation also two bands are observed at 2730 and 2810 cm^{-1} in the case of benzaldehyde. The origin of the two bands was presumed by Pozefsky *et al* (1951) to be due to the appearance of an overtone or combination band in addition to the fundamental. Recently, the splitting of C—H stretching band in aldehydes has been attributed by Bauman (quoted by Rao, 1963) to 'Fermi Resonance' of stretching vibration with an overtone of C—H bending vibration.

Table 1 Benzyl formate
Vibrational frequencies in cm^{-1}

Raman (Liquid at 28°C)	Infrared	
	Liquid at 26°C	Soln. in $CHCl_3$ at 26°C
142 (4b)D		
233 (3)P		
481 (2)P		
618 (5)P		
	694 s	695 m
	738 s	736 mb
758 (3b)	756 s	
823 (1)P	820 wsh	
862 (1)D	850 wsh	
887 (2)D	890 mb	
935 (2)P	930 w	
1000 (10)P	1000 msh	
1029 (5)P	1028 m	
	1080 m	
1158 (4)D	1155 vs	1160 vs
	1175 vssh	
1186 (4)P	1184 vssh	
1216 (6)P	1210 ssh	
	1260 s	1260 wsh
1296 (8b)P	1305 vvw	1320 w
1367 (4)D	1370 s	
1448 (2)D	1454 s	1455 w
1486 (2)P	1490 m	1495 vw
1591 (2)	1590 vw	
1609 (8)D	1602 wsh	1610 vw
1727 (6)P	1720 vs	1720 vs
	2796 wsh	
	2820 wsh	
	2850 wsh	
2892 (1)P	2905 msh	
2941 (4b)P	2950 mb	
3060 (6b)P	3060 mb	

Table 2 Benzaldehyde

Vibrational frequencies in cm^{-1}

Raman Liquid at 28°C		Infrared		
Landolt-Börnstein Table (1951)	Present authors	Liquid Garrigou-Lagrange et al. (1961)	Liquid at 26°C Present authors	Soln. in $CHCl_3$ at 26°C
126(3sb)	132 (4b)D			
+140(3sb)0.71				
225(2b)	236 (2b)D			
+237(2b) dp? (6/7)*				
447 (0) 0.40	442 (3)			
614 (5) 0.80	618 (6)D	615		
649 (3)0.54(0.10)*	649 (3)P?	648	648 s	
		686	685 s	685 m
744 (0)		741	745 vs	
828 (4)0.14	830 (4)P	826	825 vs	826 s
852 (0)				
		918		
		973		
989 (0)		990		
1000 (10)0.08	1003 (10)P	1003	1000 vw	
1022 (3)P	1022 (2)P	1023	1022 m	
		1070	1070 m	
1160 (3b)		1158		1160 msh
+1166(3b)0.36 (0.63)*	1170 (5b)D	1165	1165 vs	
1204 (7)0.25	1202 (5)P	1200	1204 vs	1204 vs
1311 (0)	1310 (2b)P	1308	1310 s	1310 m
1389 (1b)(0.36)*	1398 (0)P	1388	1392 m	1395 vw
1453 (2) 0.33 (6/7)*	1459 (1)P	1456	1456 m	1455 vw
1489 (1) 0.49	1492 (2)P	1491	1490 vw	
1583 (1)		1587		1590 m
1595 (10)0.44 (6/7)*	1601 (1)D	1598	1598 s	1600 m
1698 (8) 0.26 (0.42)*	1701 (10)P	1709	1700 vs	1700 s
2738 (1)	2735 (1)	2732	2730 m	2730 mb
		2812	2810 s	2810 vsb
3065 (6b)0.57 (0.35)*	3065 (3b)P	3065	3050 mb	

*Depolarisation factor taken from Magat's tables (1936)

Table 3 BenzoylChloride

Vibrational frequencies in cm^{-1}

Raman Liquid at 28°C		Infrared	
Landolt-Börnstein Table (1951)	Present authors	Garrigou-Lagrange et al. (1961) Liquid	Present authors Liquid at 26°C
161(3sb)+192(3b)0.15 (6/7)*	163 (3b)D		
	197 (2)D		
313(4)0.28	312 (3)P		
412(1sb) dp?(0.39)*	415 (4b)D	415	
507 (4) 0.24	507 (3)P	505	
616(5sb) 0.78	618 (4)D	617	
			650 m
671 (4b) 0.17	673 (4)P	672	672 s
775 (1) dp?	779 (2)D	772	776 s
845 (0)	840 (1)D		
874 (0)87	874 (1)D	873	870 vs
		932	
		975	
988 (1)		988	
1000 (8) 0.08	996 (2)P	1001	1002 vw
1026 (3)P	1026 (2)P	1027	1030 w
		1075	1075 wb
1162(3)+1173(4b); 0.24 (0.65)*	1170 (6b)D	1161	
		1173	1178 vs
1203 (4) 0.27	1203 (6)P	1202	1205 vs
1240 (0)	1239 (0)	1240	1244 w
1314 (0)	1315 (6b)P	1314	1320 w
1423 (0)	1427 (1)	1427	1424 wsh
1448 (1) 0.93	1448 (1)D	1452	1455 s
1483 (1) 0.81	1489 (1)P	1485	1490 vw
1581 (2)+1598(10)0.52 (6/7)*	1594 (10b)D	1581	1588 m
		1595	1601 m
1731 (2b) 0.39	1727 (4)P	1735	1730 s
1774(4b) 0.33	1770 (6)P	1777	1771 vs
3027 (0)	3026 (0)	3030	
3073 (4b)P	3060 (5b)P	3072	3058 msh
		3095	3080 mb

*Depolarisation factor taken from Magat's tables (1936)

Table 4 Assignment of the phenyl ring frequencies

Symmetry species under C_s point group	Correspondence with normal modes in benzene (Pitzer and Scott, 1943)	Vibrational frequencies of the molecules (cm)		
		Benzyl formate	Benzal dehyde	Benzoyl chloride
	20A			3080
	20B			3080
	2	3060	3065	3060
	13	3060	3065	3060
	7B			3026
	8B	1609	1601	1601
	8A	1591	1590	1588
	19A	1486	1492	1489
a'	19B	1448	1459	1448
	14	1367	1398	1427
	3	1296	1310	1315
	9A	1186	1170	1170
	9B	1158	1160*	1162*
	15	1080	1070	1075
	Breathing type mode ***(18A?)	1029	1022	1026
	p**	1000	1003	996
	6B	618	618	618
	Local oscillation*** (7A?)	1216	1202	1203
	r**	823	830	673
	6A	481	442	312
	18B	233	236	197
	17A	935	989*	988*
	5	887		874
	10A	862	852*	840
	17B	758	745	779
a''	11	694	685	685
	4		649	650
	16A			415
	16B			
	10B	142	132	163

***Sirkar and Bishui (1968a). See Text.

**Whiffen's (1956) mode for monosubstituted benzene.

*Data taken from Landolt-Börnstein Table, 1951.

Table 5 Assignment of the frequencies (in cm^{-1}) due to the substituent groups

Nature of the mode	Benzyl formate	Benzaldehyde	Benzoyl chloride
CH_2 asymmetric stretching	2950		
CH stretching (due to the formyl group and the aldehyde group)	2941	2810 2735	
CH_2 symmetric stretching	2892		
C = O bond stretching	1720	1698	1774 1731
CH_2 scissoring	1454		
In-plane CH deformation (due to the formyl group)	1370		
CH_2 wagging	1260		
C—O stretching	1175		
CH_2 twisting	1155		
Out-of-plane CH deformation (due to the formyl group)	1028		
CH_2 rocking	738		
C—Cl stretching			507

(iii) *Other vibrations* : The very strong infrared band at 1175 cm^{-1} which appears as a shoulder in benzyl formate is assigned to the C—O stretching mode. Benzoyl chloride exhibits a polarised Raman line at 507 cm^{-1} while the other two compounds do not yield any line in similar position. This line has, therefore, been taken as representing the C—Cl stretching vibrational frequency, though the value appears to be somewhat low. It may be noted that Lecomte (1936) and Sheppard (1949, 1950) observed that the C-Cl stretching frequency falls off to low value of 570 cm^{-1} when the group is attached to the tertiary carbon atoms.

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